Determination of Pectin Grade of Apple Pomace

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APPLE pomace is dried in the hope of disposing of it profitably for pectin manufacture. If the dried pomace is of satisfactory quality, it is sold for that purpose; if not, it is sold for cattle feed at a price which rarely pays for cost of production. This laboratory is studying factors affecting the quality of commercial pomace in an effort to preserve its pectin value.

The method described here for the evaluation of apple pomace should be useful in determining its probable market value, in learning the cause of low grade pomace, and in formulating methods for improving its quality. It should also be helpful in separating pomace into a "pectin" grade and a "cattle feed" grade according to quality, in preference to blending poor with good pomace to make a product of uniform but mediocre quality. The pomace manufacturer usually depends upon the customer's evaluation, and often he learns of the low quality of the product too late to determine the cause or make corrections. Methods used to evaluate pectin quality vary and are relatively unknown to the pomace manufacturer.

Chemical analysis of pomace for pectin does not evaluate its usefulness for jelly making, since it does not take pectin grade into consideration. A method of evaluation is needed that actually measures the quality upon which the value of pomace is based—its capacity to make jelly. Such a method should show the quality as well as quantity of pectin present. Viscosity measurements of pomace extracts have only limited value in approximating jellying capacity because this property is subject to many influences, such as the presence of starch and other non-pectin colloidal material, the presence of salts, especially those of calcium and magnesium, the concentration, molecular weight, and degree of esterification of the pectin, thixotropic effects, and pH and temperature. To evaluate pomace properly it is therefore necessary to prepare jellies under carefully controlled conditions which simulate those in commercial jelly making.

The method of evaluating pomace described herein consists in preparing an extract under a stated set of conditions of time, temperature, pH and reagents, and then making a 65 percent sugar jelly from this extract by a fixed procedure. Results are reported as "grade" of the pomace. This has the same meaning as when applied to commercial pectin, that is, it is the number of units (pounds) of sugar that can be made into a jelly of standard firmness by the pectin in one unit (pound) of pomace. Thus it also indicates the percent of 100 grade pectin potentially extractable from the pomace. A good pomace gives a 25 to 35 grade by this method, a medium one 18 to 25, and a poor one less than 18, these values being without correction for moisture.

The total amount of pectin is determined rather than that in just the extraction liquor. No correction is made for the residue of press cake, but dilution is made on the basis of total weight. The proportion of pomace to extract is regulated to avoid in most cases concentration of the extract before preparing the jelly. The pH of extraction is near that at which pectin is most stable. The use of sodium tetraphosphate as an extractant simplifies pH adjustment, as a greater pH range (3.0-3.4) is permissible and the pH is near that required for jelly making.

Procedure

Materials and Equipment Required:

Sodium tetraphosphate ($Na_6P_4O_{13}$).

Buffer solution A: 8.5 g. citric acid and 8.5 g. sodium citrate made up to 100 ml. of solution.

Buffer solution B: 40 g. citric acid and 5 g. sodium citrate made up to 100 ml. of solution.

Sodium hydroxide solution, 0.5 N.

Sulfuric Acid, 0.5 N.

Hydrochloric acid, 1 vol. concentrated + 9 vol. water.

Capillary viscosimeter, Ostwald-Cannon-Fenske No. 300.

Electric heater with rheostat such as 550 watt "Precision."

Jelly tester, Delaware or Tarr-Baker jelly strength tester.

Mechanical stirrer, air-driven piston type or gear-drive electric motor driven.

Glass electrode pH meter.

Refractometer or Brix spindle.

Jelly glasses, tall form, smooth sides (or Griffin type 250-ml. Pyrex beakers).

Wiley mill, or similar grinder.

Hydraulic press.

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Preparation of Extract: In tared 500-ml. wide-mouth Erlenmeyer flasks mix duplicate 30-g. samples of dry pomace (ground through a 2-mm. screen in a Wiley mill) with 1.2 g. of sodium tetraphosphate ($Na_6P_4O_{13}$). Add 300 to 400 ml. of boiling distilled water, depending on the grade of the pomace, and 4 to 7 ml. of dilute (1 + 9) hydrochloric acid. Using a glass electrode pH meter determine the pH five minutes after adding the acid and if necessary adjust to pH 3.2 ± 0.2. Maintain the extraction mixture at 90° ± 2° C. for 75 minutes. Cool to 70° C., determine the net weight of the extraction mixture, and press in a coarse muslin or light crash press cloth, preferably in a laboratory hydraulic press at 140 pounds per square inch on the cloth (3,600 pounds load on a 5 by 5-inch cake). Adjust the pH of the extract to 3.2 ± 0.1 by stirring into it 0.5 N acid or alkali. Determine soluble solids by a refractometer or Brix spindle and the relative viscosity at 25° C. using a fast-flowing capillary viscosimeter such as an Ostwald-Cannon-Fenske No. 300.

Preparation of Test Jelly: Weigh into a tared 400-ml. beaker the amount of pomace extract specified for the relative viscosity in Table I that corresponds most closely with the viscosity determined on the extract.

TABLE I

Weight of Various Grades of Pectin Extract Required for a Standard Strength Jelly

Relative viscosity of extract at 25°C, pH 3.2, starch not removed	Assumed grade of extract	Weight of extract required for standard jelly (g.)	
9	1.0	135	Concentrate, or prepare less-than-standard-strength jelly
10	1.1	123	
11	1.2	112	
12	1.3	104	
14	1.4	96	
16	1.5	90	
18	1.6	84	
20	1.7	79	
23	1.8	75	Add water to make a total weight of 80 g.
26	1.9	71	
30	2.0	68	
33	2.1	64	
38	2.2	61	
43	2.3	59	
48	2.4	56	
54	2.5	54	

Add to the extract in the beaker 1 ml. of buffer solution A and heat the pectin solution nearly to boiling in about 2¼ minutes while stirring with a mechanical stirrer. If a 550-watt "Precision"-type electric heater with built-in rheostat is used, the 400-ml. beaker should rest directly on the porcelain holder of the heating element. Add 135 g. sugar (less weight of soluble solids contained in the extract as shown by refractometer or Brix spindle) slowly to the pectin solution while it is being heated and stirred. The pectin solution must be kept hot during the addition of sugar, and the sugar must be added in a slow stream over a period of one minute to avoid jelly formation in the beaker. As soon as all the sugar has been added, return to a boil and then adjust to a net weight of 208 g. by adding water or by further boiling. Remove from the heat occasionally and weigh; otherwise, too much water may be evaporated. If water is added to restore the weight, heat again until boiling begins. When the correct weight has been reached, remove the beaker from the heat and allow it to stand for 30 seconds. Skim off the foam that rises and pour the hot liquid into a previously prepared jelly glass containing 3 ml. of buffer solution B. Stir for about 5 seconds with a glass rod so that the buffer and hot solution are thoroughly mixed. Place the lid loosely on the jelly glass until the sensible heat is lost, then cover tightly.

After allowing the jelly to stand at room temperature (20 to 25° C.) for 18 to 24 hours, turn it out of the jelly glass on to a glass plate or Petri dish and determine the strength on a Delaware jelly tester(1). As a routine check on technique one should determine the soluble solids of the jelly by means of a refractometer, and the pH using a glass electrode pH meter. The soluble solids should be 65.0 ± 1.0 per cent and the pH 3.0 ± 0.1. The grade of the pomace is calculated by the following procedure. From the strength of the jelly as determined on the Delaware jelly tester find the ratio of the true grade from the calibration curve of the jelly tester as shown in Fig. 1 (see below under calibration of jelly tester) and multiply this ratio by the assumed grade of the extract used to select the quantity to make the test jelly (Table I) to obtain the true grade of the extract. Then the true grade of the extract is multiplied by the weight of the extraction mixture and divided by the weight of the sample to obtain the grade of the pomace.

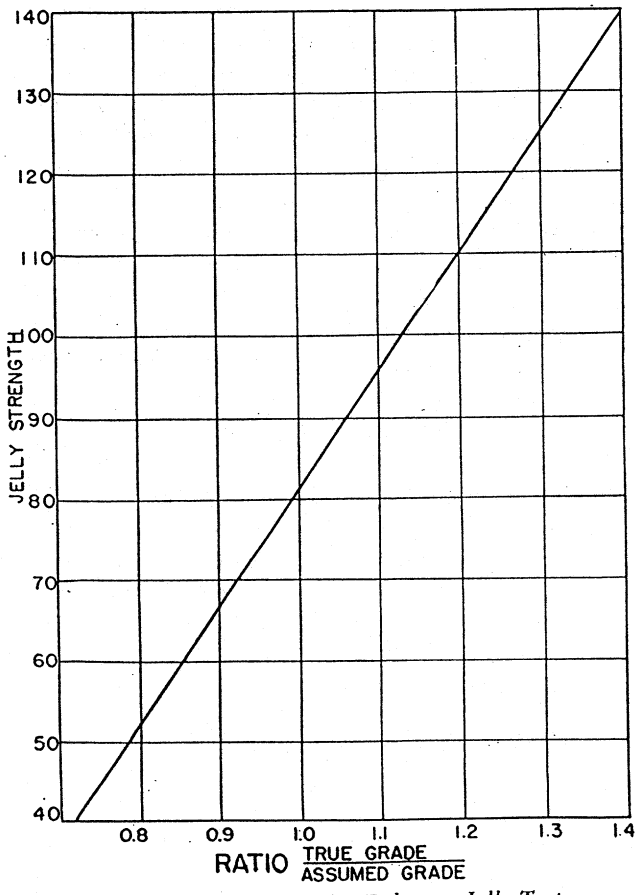

Fig. 1. Calibration Curve for Delaware Jelly Tester, $\frac{\text{true grade}}{\text{assumed grade}}$ vs. Strength

Sample Calculation: A 30-gram sample of pomace was extracted. The extraction mixture weighed 328 g. The relative viscosity of the extract was 35. From Table I a grade of 2.1 was assumed, and 64 g. of extract was used in making test jellies. These jellies had an average strength of 71 cm., which, from Fig. 1, gives a ratio to a standard strength jelly of 0.93. The true grade of the extract was therefore 2.1 x 0.93 or 1.95. Applying this to the extraction mixture, $1.95 \times \frac{328}{30} = 21.3$, the grade of the pomace.

Discussion of Procedure

Preparation of Sample: Since pomace varies greatly in pectin value, a sample must be selected carefully to make sure that it is representative. Grinding through a 2 mm. screen in a Wiley mill is necessary for uniformity of sample as well as to accomplish complete liberation of the pectin during extraction. In assaying a commercial sample, it is customary not to correct for moisture content. A more accurate appraisal of results requires correction to a moisture-free basis.

Conditions of Extraction: By using between 300 and 400 g. of water in extracting a 30-g. sample an extraction ratio, $\left(\frac{\text{wt. of extraction mixture}}{\text{wt. of sample}}\right)$, between 11 and 14 is obtained. The quantity of water is selected on the basis of the probable grade from either a knowledge of the history of the sample or previous analyses. This yields an extract which can be used to make test jellies in most cases without adjustment of volume. If the assumed grade of the extract is less than 1.5 and hence the quantity required for a standard strength jelly is greater than 90 g., a jelly of less than standard strength may be prepared by using 90 g. with an assumed grade of 1.5. If the extract is very dilute it may be weighed into a tared flask, concentrated under vacuum, and again weighed to determine the ratio of concentration, and a jelly made from a weighed portion of the concentrated extract. When less than 79 g. of extract is indicated, distilled water is added to make a total weight of 80 g.

Buffers: The buffers are those listed in the mimeograph "FSCC Specifications for 'Commercial Pectin Preparation (Food)'" of September 8, 1942,[3] except that buffer solution A is made up at half the strength specified in the mimeograph, to avoid precipitation of salts from the concentrated solution on standing. Twice the relative volume is therefore used in preparing the jelly. The less acid buffer, solution A (pH 3.9), is added to the pectin solution. The more acid buffer, solution B (pH 2.2), is placed in the jelly glass and mixed while pouring. The mixture of the stated amounts of buffer solutions A and B has a pH of 2.9, which compensates for slightly higher pH values in pectin and pomace extracts and gives a jelly of pH 3.0 ± 0.1. The buffers are present in 0.15 molar concentration in the finished jelly.

[3] Obtainable from Processed Products Standardization and Inspection Division, War Food Administration, Washington 25, D. C.

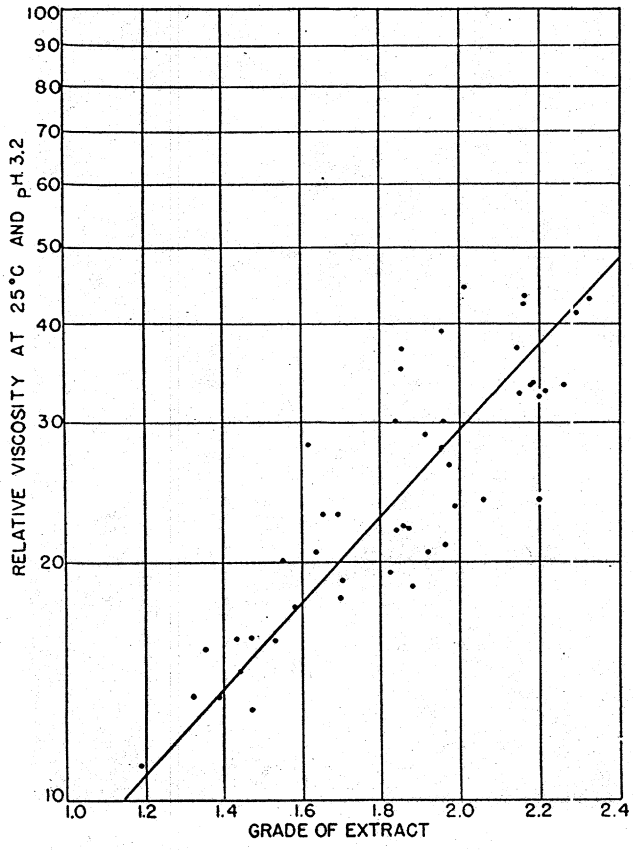

Fig. 2. Relative Viscosity vs. Grade of Pomace Extracts.

Viscosity: The values for grade and viscosity in Table I were obtained from the graph in Fig. 2, which represents a plot of the logarithm of the relative viscosity vs. grade of extract by actual jelly tests on a large number of pomace extracts. The graph was developed not for determining grade but to enable selection of a test grade which would assure a jelly of near standard strength. An attempt at closer approximation of grade by viscosity measurements would require removal of starch and elimination of other disturbing influences. Although in some cases wide variations from the curve are noted, jellies of measurable strength were obtained in all instances.

Jelly Testing: The conditions used for making test jellies were essentially those specified in the mimeograph "FSCC Specifications for 'Commercial Pectin Preparation (Food)'," except that only 27 percent of the quantities were used. This amount filled one jelly glass and facilitated the use of replicates on the jelly-making technique rather than on the strength measurement alone. The use of an objective test for jelly strength lessens the need for making multiple tests on jellies from the same batch.

Various characteristics of jellies have been measured as representative of strength. Cox and Higby (2) used rigidly or elastic modulus as determined by per cent sag in the turned-out jelly. The elastic modulus is also measured by the B.A.R. jelly tester (3). Because of differences in elasticity, we preferred to measure the breaking point, as is done by the Delaware jelly tester (1). This instrument (Fig. 3) measures the force, in centimeters of water, required to break the surface of a jelly by a plunger; the force is sup-

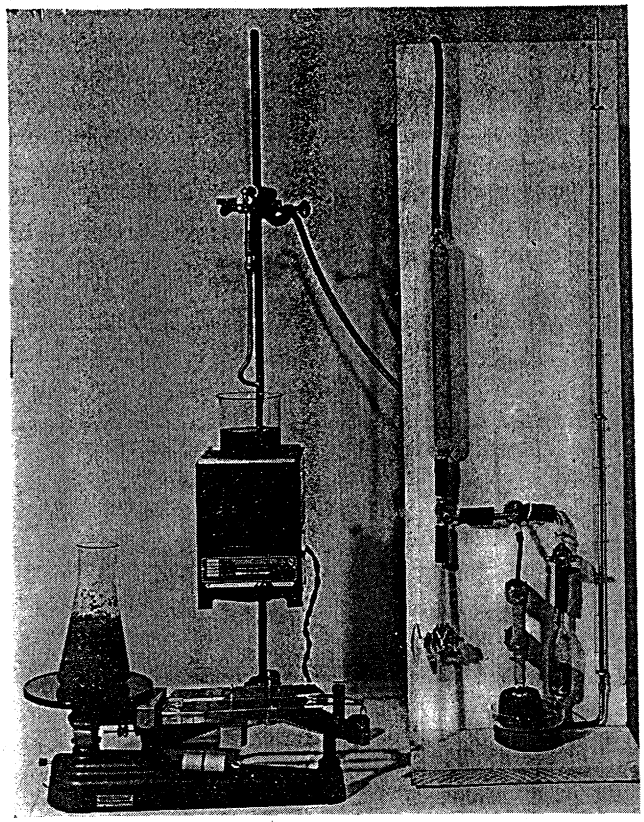

Fig. 3. Equipment Used in Pomace Grade Determination.

plied by air pressure; the plunger is an ordinary hypodermic syringe. It must be calibrated with pectin of accepted grade through a range that will include jellies considerably above and below standard strength. The elastic modulus of jellies can also be determined with this instrument by using the volume calibrations on the hypodermic syringe.

The hydrostatic pressure reading on a Delaware jelly tester depends on the ratio between the area of the head or cap which penetrates the jelly and that of the syringe plunger. Any usual ratio appears satisfactory with a calibrated instrument, but an unqualified reading on an uncalibrated instrument suffers in meaning. The actual dimensions in our instrument are shown in Fig. 4.

To determine the effect of contour, stainless steel caps with varying degrees of rounded end-profile were tried. A square-cut cap cut out a disc, and a well-rounded cap produced a crack in the jelly. Both gave low readings. The one having the edges slightly rounded to conform to the contour of the jelly surface under pressure of the tip gave the highest reading and was selected for use in the experiments reported herein. Later it was noted that the glass tip of the syringe approximates this contour and it has been satisfactorily used without a metal tip.

Air was used to build up pressure in the system to the breaking-point of the jelly. The laboratory air supply (85 pounds) was reduced to 4 pounds per square inch by a ¼-inch reducing valve, and was controlled by a ⅛-inch needle valve adjusted to give the required rate of increase in the height of water in the manometer (50 to 70 cm. in 60 sec.). The needle valve was left open at this setting,

TABLE II

Quantity of Pectin of Various Grades Required for a Standard Strength Jelly

Assumed Grade	Weight (grams)	Assumed Grade	Weight (grams)
50	2.70	140	0.96
60	2.22	150	0.90
70	1.93	160	0.84
80	1.69	170	0.79
90	1.50	180	0.75
100	1.35	190	0.71
110	1.23	200	0.68
120	1.12	210	0.64
130	1.04	220	0.61

and pressure was built up in the system by closing the stopcock on the storage vessel. At the end of the test, this stopcock was opened and left in this position. In later tests carbon tetrachloride colored with a little Sudan IV has been used in the manometer, reducing the height of the manometer tube.

Calibration of Jelly Tester: Various pectin manufacturers and research investigators have different concepts of a standard strength jelly. We based our standard on a sample[4] supplied by the Processed Products Standardization and Inspection Division of the War Food Administration, Washington 25, D. C. This standard was accepted as a basis of sale by various suppliers of pectin for Lend-Lease purposes. The jelly tester was calibrated with a series of jellies using the amount of pectin corresponding to the stated standardized grade shown in Table II, and the amounts corresponding to grades 10, 20, and 30 percent above and below the standardized grade. The pectin was weighed into tared 400-ml. beakers and dispersed with the aid of 2 ml. of 95 percent alcohol or by mixing in 4 or 5 g. of sugar from the 135-g. weighed portion to be used in the jelly. Seventy-five ml. of cold distilled water and one ml. of buffer solution A were added, and the procedure given for making a test jelly from the pomace extract was followed. The strengths of the

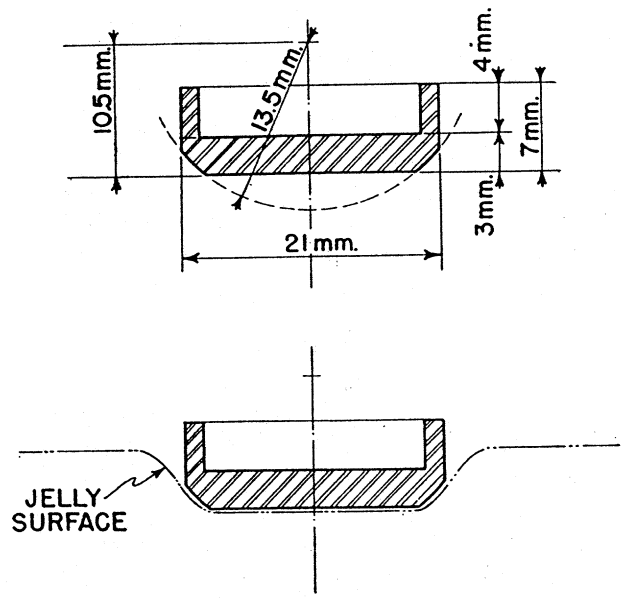

Fig. 4. Machined Tip for Jelly Tester Showing Area of Contact.

[4] This material is no longer available.

jellies were determined and plotted against the factor $\frac{\text{true grade}}{\text{assumed grade}}$ in the same manner that Cox and Higby(2) have done for the "ridgelimeter." The factor to be applied to a test jelly for correction to standard strength can be determined by inspection of the curve so obtained, thus eliminating the necessity of making a number of jellies in order to approach a standard strength jelly. The calibration curve for our jelly tester, shown in Fig. 1, indicated a reading of 82 cm. of water for a standard strength jelly.

Additional work on jelly testing prompts us to recommend the use of 250-ml. Pyrex beakers instead of jelly glasses to mold test jellies. They are more uniform in dimensions, being machine-molded by one manufacturer. Objective testing and the use of beakers and mechanical stirrers in place of cooking pans and ladles are less suggestive of a "Kitchen" method.

Uses of the Method

Evaluating Commercial Pomace: There is no basis for direct comparison of grade values for pomace obtained by our procedure with those obtained by most pectin manufacturers. Although it is not feasible to evaluate a pomace on the basis of each manufacturing process, as extraction procedures vary too greatly, we believe that the proposed method will indicate relative yields by any process of manufacture. In general, high pectin yields will be obtained from lots showing high values (25-35 grade). Leaching of the test sample is considered inadvisable because there is no standard leach treatment.

Table III shows the results of applying the method to a few samples of commercially dried pomace. Trade acceptance paralleled the quality of the pomace shown by these results. For example, that represented by No. 6 was judged to be inferior by the would-be purchaser, who offered only 50 percent of the market price for it. Manufacturers of Nos. 1, 3, 4, 5, and 7 found a ready sale for their product. The manufacturer of No. 5 stated that the pectin value of this pomace was considered good but objection was made to the color.

TABLE III

Pectin Grade of Commercially Dried Apple Pomace

Sample No.	Description	Determined Grade	Moisture	Acceptance by Purchaser
1	Peels, cores, and <2¼" York, single pressed, Roto-Louvre dried. Early season 10/16/44.	36	4.2	Readily accepted
2	Peels, cores, and <2¼" York, twice pressed, rotary steam tube dried, 10/17/44.	16	1.5	Accepted but called "Low Quality"
3	Peels, cores, and <2¼" York, twice pressed, kiln dried, 10/17/44.	30	0.7	Readily accepted
4	Pomace from whole cider apples, twice pressed, dried on belt drier, 10/30/44.	30	8.0	Readily accepted
5	Peels, cores, and <2¼" York, twice pressed, rotary steam tube drier.	30	5.0	Accepted, called "Good"
6	Pomace from whole cider apples, single pressed, kiln dried, 11/1/44.	16	4.8	Discounted 50%
7	Pomace from sharply culled juice grade Jonathan, single pressed, kiln dried, 10/16/44.	31	3.6	Readily accepted, but color objectionable

Processing Studies: In applying the method to processing studies, the limitation of its accuracy must be kept in mind. The error in making and testing jellies is possibly 5 percent, even when an objective test is used to determine the strength of the jelly. The overall error of this method of evaluating pomace is probably 10 per cent. In view of the known variation in raw material, the sampling error is considered to be large. Because of these factors, only gross differences can be detected with a limited number of samples.

Table IV shows the results of applying the method to determine the desirability of applying forced recirculation to the operation of a kiln-type drier. A greater degree of preservation of the pectin value is indicated for this type of operation, which resulted in an average grade of 28, as compared with 22 for natural convection.

TABLE IV

Grade of Pomace Obtained in Kiln with Various Types of Air Circulation. (Single pressed pomace from closely graded juice varieties, advanced maturity.)

Air Circulation	Grade (moisture-free basis) Dried 11/21/44	Dried 12/26/44
Natural convection	21	23
Forced circulation, low draft	24	23
Forced recirculation, strong draft	28	28

Table V gives the results of a comparative study of commercial drying operations. Since it is not feasible to dry the same lot of pomace in different types of large-

TABLE V

Grade of Pomace Obtained by Various Commercial Driers and by Laboratory Through-Circulation Drier

Sample No.	Description	Grade (moisture-free basis) Commercially dried	Laboratory dried
1	Pomace from peels, cores, and <2¼" York, single pressed, Roto-Louvre dried, 12/14/44.	32	27
2	Dried under same conditions as No. 1; sample taken 2 hours later.	33	30
3	Pomace from peels, cores and <2¼" York, twice pressed. Rotary steam tube drier operated under 90 pounds steam pressure, 12/15/44.	16	17
4	Dried under same conditions as No. 3; sample taken 2 hours later.	17	19
5	Pomace from peels, cores and <2¼" York, twice pressed. Rotary steam tube dried operated under 20 pounds steam pressure, 12/15/44.	29	25
6	Dried under same conditions as No. 5; sample taken 2 hours later.	26	28
7	Single-pressed pomace from closely graded juice varieties; advanced maturity. Kiln drier with forced circulation, 11/30/44.	32	31

scale commercial driers, a laboratory through-recirculation drier was used to dry small samples of the wet pomace being dried in each of the commercial driers. These samples were dried immediately, and comparable samples were taken from the commercial run when it was estimated that the same material was being discharged. The low original quality of the pomace supplied the rotary steam tube drier using 90 pounds' steam pressure is shown by the samples of Nos. 3 and 4 dried in the laboratory drier, proving that the cause of the low quality of pomace at this plant is not due alone to drying conditions.

Testing Liquid Pectin: The pomace extract test is applicable to liquid pectin. The method may be used to detect loss of grade during steps in pectin manufacture such as in the treatment of liquid pectin with commercial diastase preparations to remove starch. As many diastase preparations contain a pectin-degrading enzyme, selection of such a preparation should be based on the minimum loss of grade under the conditions used. The test is also useful for control work in the manufacture of pectin. The degree of concentration necessary to yield a concentrated liquid pectin of the desired grade may be calculated from a test jelly made with filtered pomace extract, allowance being made for losses during vacuum evaporation. Concentrated liquid pectin may be evaluated by this method, but viscosity measurements are too unreliable in this case to be used as a guide. For 5 grade liquid pectin a 27-g. sample is taken. Standard liquid pectin, one gallon of which jellies 50 pounds of sugar, corresponds to 5.7 grade and requires a sample weighing 23.6 g. for a standard jelly. "Certo" liquid pectin had a grade of 6.7 by our test.

Grading Dry Pectin: The procedure used to calibrate the jelly tester can also be used to grade dry pectin. A quantity of pectin is taken corresponding to its assumed grade, as shown in Table II, and a jelly is prepared as described in the calibration of the jelly tester.

Summary

A METHOD is given for evaluating apple pomace by preparing an extract, making a test jelly, and determining the strength of the jelly on a calibrated Delaware jelly tester. The results, reported as "grade," represent the percent of 100 grade pectin available in the pomace. The method has no counterpart in the present empirical methods of evaluating commercial pomace for pectin manufacture, but results obtained do parallel trade acceptance of lots tested, suggesting its use in selecting high-quality pomace. The method should prove a valuable tool in research studies aimed at improving the quality of commercial pomace. The jelly-making procedure can be used in control work in pectin manufacture and in evaluating commercial samples of both liquid and dry pectin.

The extent to which pomace manufacturers will find a profitable market, in spite of expanded citrus pectin production, depends in part on their ability to produce high quality pomace. This procedure for evaluating pomace has been helpful in studies aimed at raising the pectin grade. Pectin manufacturers are in the best position to determine whether or not it has value in selecting high quality pomace.

Acknowledgment

Thanks are due manufacturers of pomace, too numerous to mention individually, who cooperated in furnishing samples and detailed information on drying conditions in their plants.

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